

Reversible Cathode Reaction of Disulfide Ligands in Metal-Organic Framework Revealed by S *K*-edge XAFS Analysis

Takeshi Shimizu¹, Hirofumi Yoshikawa¹, Masashi Yoshimura², Koji Nakanishi², Toshiaki Ohta²

1) Graduate School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen Sanda, Japan

2) Research Organization of Science and Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi Kusatsu 525-8577, Japan

1. Introduction

Development of alternative rechargeable batteries to the present Li ion batteries, in which LiCoO₂ is used as cathode active materials, is one of the most important issues due to ever-increasing energy demands and pressing environmental concerns. Recently, metal-organic frameworks (MOF) have attracted much attention as promising cathode materials since they exhibited a high capacity during multiple cycles due to their robust frameworks and dual redox reactions of metal ions and organic ligands^[1]. We also found that MOFs including 4,4'-dipyridyl disulfide (4dpds) ligand, [Cu(oxalate)(4dpds)]_n (S-MOF), exhibited a high capacity based on one- and two-electrons redox of Cu ions and 4dpds, respectively (Figure 1), and a stable cycle performance, although disulfide compounds usually show a poor cycle performance because of S-S bond cleavage during discharge process. In this work, we attempted to reveal this battery reaction mechanism by using S *K*-edge XAFS analysis.

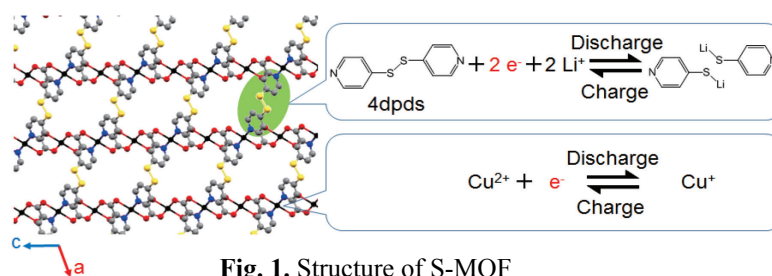


Fig. 1. Structure of S-MOF

2. Experimental

Two-dimensional S-MOF was prepared according to the literature^[2]. We fabricated thin film cathode composed of 30 wt% S-MOF, 60 wt% carbon black and 10 wt% PVDF on Al foil, and then coin cell batteries were assembled by using the cathode, lithium foil as an anode and 1 M LiPF₆ in tetraethylene glycol as an electrolyte. To investigate the cleavage/recombination mechanism of S-S bond in 4dpds of S-MOF during discharge/charge process, *ex situ* S *K*-edge XAFS measurements of cathode samples, which were taken out of the coin cells stopped at various battery voltages during charge/discharge tests, were performed using a KTP (011)

crystal pair at the soft X-ray double crystal monochromator beamline, BL-13, in the SR Center of Ritsumeikan University. The spectra were taken in partial fluorescence yield (PFY) mode.

3. Results and Discussion

Figure 2 shows discharge/charge curves of the S-MOF battery. In the second discharge curve, we obtained a high capacity of 175 mAh g⁻¹ with two plateaus around 2.8 V and 2.6 V, which indicate reduction of Cu ions and disulfide ligands, respectively, while similar behavior was observed in the charge curves with higher voltage plateaus. The capacity retention was 84.4 % after 20 cycles.

Figure 3 shows *ex situ* S *K*-edge XANES spectra of S-MOF cathode samples. Two distinct peaks at 2472 and 2474 eV were observed in the pristine cathode. The lower energy peak can be assigned to the transition from 1s to σ^* (S-S), while the higher one is associated with that from 1s to σ^* (S-C)^[3,4]. After discharging (1D), the lower energy peak disappeared, which suggests the cleavage of S-S bonds in 4dpds ligand of S-MOF. Then, the original doublet peak was recovered after charging (1C), while it returned to a single peak after re-discharging (2D). This phenomenon indicated a reversible recombination and cleavage of S-S bonds in 4dpds ligands of S-MOF. It is suggested that the robust framework of MOFs enabled S-S covalent bonds in ligands to be cleaved and recovered reversibly in the electrochemical reaction, which resulted in a high capacity and a stable cycle performance.

References

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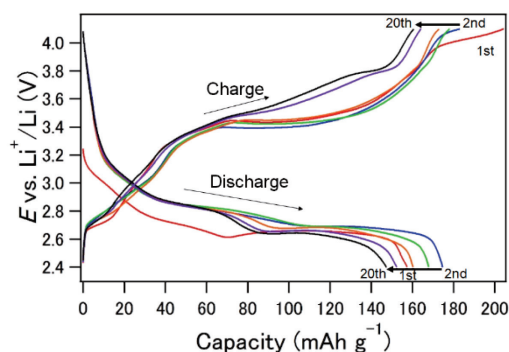


Fig. 2. Discharge-charge curves of the S-MOF battery during 20 cycles

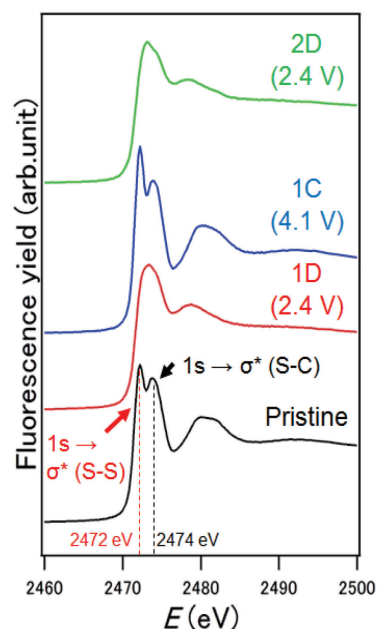


Fig. 3. *Ex situ* S *K*-edge XANES spectra of cathode samples of the S-MOF batteries.